Analyses of some bismuth minerals.

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We have very small data referring to some Bi-Te minerals, especially to joseite and grünlingite. The few number of data is not only due to the want of interest but chiefly to lack of subjects to be investigated. As we have a collection in our institute containing very pure bismuth minerals from *Rézbánya (Baia)* and *Csiklova (Ciclova)* I am able to give new data of analyses of some bismuth minerals.

The methods for determining each component were combined so that all of the components should be established from one weighing as I had very little pure material in most cases. For decomposition of Bi-Te minerals *Clauder* (1) recommend the decomposition by chlor gas, but the S content is established from a new weighing after decomposition by a mixture of aequal portion of $KMnO_4$, Na_2CO_3 and MgO according to Gedeon. *Antal* (2) similarly determines the S content from a separate weighing according to Fresenius. He decomposed tetradymite for determining of the Te and Bi with HNO_3. He recommends for decomposition of bismuthine nitric acid and bromine. *Koch* (3) dissolved bismuthine, cosalite and rézbányite in concentrated HCl and determined the S content also from a separate weighing. The determination of bismuth was generelly carried out in form of BiOCl and the determination of Te was made either after reduction by d-glucose in basic medium or after precipitation in form of crystalleous metal Te according to Clauder's method (1).

I used aqua regia for decomposition of joseite, grünlingite and a Bi-Te mineral which has not been described up till now. The decomposition of tetradymite, cosalite was carried out by nitric acid + bromine. If, in spite of careful decomposition by aqua regia, S fell out of solution, I oxidised with a few drops of the bromine.

The oldest method for precipitation of Te is the precipitation by SO_2 in acidic medium. The precipitation is carried out by the conducting of SO_2 gas, or by concentrated solution of Na_2SO_3. (References referring to methods of precipitation of Te under 1. p. 8.) I intended the precipitation of Te also by reduction. But on adding the precipitating reagent the solution becomes dilute, to avoid this and the conduction of gas, the precipitation was made by solid Na_2SO_3. The HCl content of solution containing Bi and Te was adjusted to a percentage of about 10—12 before precipitation as the optimal concentration of free HCl for precipitation of Te is between percentages of 7—15 (4). I added few solid Na_2SO_3 to the cold solution of 80—100 ml, then I repeated this procedure with small portions until I had no a penetrating smell of SO_2. One has to use tall form beaker and to cover it to avoid loss on account of foaming. The colour of solution in a water bath becomes forst bluish grey, then dark and after perfect falling out of Te quiet clear. The precipitate of metal Te is well filtrable by sintered-glass filter crucible No. G. 4., or porcelain filter crucible No. A. 2. For washing of the precipitate I used first HCl of 10—12 percentage, afterwards

a little hot distilled water and at last heving washed by aethanol I dryed in an electric drying oven at a temperature of 110° C for one hour.

If Te and Se were also to be determined I put the solution immediately after decomposition and filtrating of the insolubile rest into a volumetric flask and filled it. I immediately coprecipitated Te and Se from one portion and after coprecipitation of Bi and Te I determined Te alone. The difference between the two weighings gives the Se content.

Joseite — Bi_3TeS (Rézbánya — Baita):

A contribution of analyses of joseite and grünlingite is given by *Damour* (1845), *Genth* (1880) and *Mingaye* (1916). The same results are mentioned by *Doelter* and *Hintze* (5., 6.). The same data are to be found in the Te volume of Gmelins Handbuch published 1940 (7).

The joseite used for investigation was pure and free from impurities excepting a minimal native Bi along the lamellae. The specific gravity is 7.68, 7,79 according to references and 7.66 according to my own results. My substance contained according to qualitative analysis: Bi, Te, S.

The procedure was the following; The decomposition was carried out by aqua regia. After perfect dissolving the solution was carefully evaporated. After adding sufficient quantity of HCl I dissolved it in hot water. I coprecipitated Bi and Te with NH_4OH, $(NH_4)_2CO_3$. The filtrate was evaporated. The evaporation was repeated after adding a few drops of HCl and the S content was determined as $BaSO_4$ according to Winkler. The precipitate of Bi and Te was dissolved in hot dilute HCl (the presence of nitrates is to be avoided at precipitating of Te) provided a free HCl content of about 10—12%. I separated Te according to the above mentioned, method, then I determined Bi from the filtrate of Te, precipitating formerly by NH_4OH and $(NH_4)_2CO_3$ and after dissolving this precipitate in dilute warm nitric acid according to Antal.

The results of analyses are:

		Weight%	Atomic ratio.	
	Bi	80.10%	0.3832	3.16
I.	Te	15.46	0.1211	1
	S	4.55	0.1419	1.1
		100.11%		

		Weight %	Atomic ratio.		Calcul. comp.
	Bi	79.96%	0.3826	3.17	) 79.70%
II.	Te	15.40.	0.1206	1	16.22
	S	4.47	0.1395	1.15	4.08
		99.83%			100.00%

On comparing the results of old and new analyses we find that the composition of joseite — in accordance with the opinion up till now — is Bi_3TeS. My data and results of other researches agree well. (The mean value of old results is: Bi 79.59%, Te 15.42%, S (Se) 4.50%.)

Grünlingite — Bi_4TeS_3 (Rézbánya — Baia):

We have fewer data referring to grünlingite. The first result is given by *Muthmann* and *Schröder* (1897). *Garrido* and *Feo* (8) refer to the results above mentioned in 1938. The specific gravity of grünlingite is 7.32 according to *Doelter* (5) and 8.15 according to *Peacock* (9). I found the specific gravity of my substance 8.34. The qualitative analysis gave: Bi, Te, Se, S.

The procedure is the same as in the case of joseite excepting that here the Se content had also to be determined from filtrate of precipitate of Bi and Te.

The analyses gave:

		Weight %	Atomic ratio.		
I.	Bi	77.82%	0.3723	0.3723	3.6
	Te	13.09	0.1025	0.1025	1
	Se	0.58	0.0073	0.2915	2.8
	S	9.11	0.2842		
		100.60%			
II.	Bi	78.22%	0.3742	0.3742	3.8
	Te	12.45	0.0975	0.0975	1
	Se	1.17	0.0148	0.2718	2.78
	S	8.24	0.2570		
		100.08%			
III.	Bi	78.22%	0.3742	0.3742	3.74
	Te	12.84	0.1006	0.1006	1
	Se	1.12	0.0141	0.2711	2.7
	S	8.24	0.2570		
		100.42%			

For comparing I give the results of the two old analyses:

	I.			II.		
Bi	78.82%	0.3771	3.8	79.31%	0.3794	3.77
Te	12.66	0.0992	1	12.82	0.1004	1
S	9.40	0.2932	2.9	9.31	0.2904	2.89
	100.88%			101.44%		

Brugger also carried out some investigations referring to my substance in 1943. His results, which are not yet published, are:

Bi: 78.25, 77.80 and 79.08%
Te: 12.50, 12.87, 12.78 and 12.86%

The presence of Se was also determined by him but not quantitatively. In the results of old analyses no mention is to be found about Se.

The formula of grünlingite is Bi_4TeS_3 taking into consideration any result.

The substance to be investigated was carefully selected. The microscopical investigations of polished section of ore showed that both joseite and grünlingite were perfectly homogeneous. One of the polished section of joseite was used for analysis therefore it is sure that the result of analysis refer to a homogeneous substance.

Bi_6TeS_4 (Rézbánya — Baita):

Koch (10) investigated a sample collected in Rézbánya. A homogeneous bismuth telluride appeared in the polished section which differed in darker colour from joseite and grünlingite. The result of analysis showed that it differs from joseite and grünlingite as regards its composition as well as its optical properties.

The procedure of analysis is the same as in the case of joseite. The result of qualitative analysis is Bi, Te and S.

I could select only a very small amount of pure substance. The weighing was 0.0904 g in the first case, 0.0846 g in the second one, and 0.0784 g in the last case when only the Te content was to be determined.

		Weight %	Calculated to 100%	Atomic ratio.	
I.	Bi	81.58%	81.87%	0.3916	5.75
	Te	8.65	8.68	0.0680	1
	S	9.42	9.42	0.2948	4.33
		99.65%	100.00%		
II.	Bi	81.76%	82.51%	0.3947	5.48
	Te	9.10	9.18	0.0719	1
	S	8.23	8.31	0.2592	3.6
	imp.	1.12			
		100.21%	100.00%		

The result of the separate analysis of Te: Te ..... 9.18%.

Calculating the atomic % we receive:

	I.	II.
Bi	51.92%	54.39%
Te	9.00	9.90
S	39.08	35.71
	100.00%	100.00%

Taking the mean value of analyses the result is:

	Weight %	Atomic ratio.		Atomic %
Bi	82.04%	0.3926	5.61	53.09%
Te	8.93	0.0699	1	9.46
S	8.88	0.2770	3.95	37.45
	99.85%	0.7395		100.00%

The ideal composition of Bi_6TeS_4 is:

	Weight %	Atomic ratio.		Atomic %
Bi	83.05%	0.3974	6.00	54.53%
Te	8.45	0.0622	1	9.08
S	8.50	0.2651	4.0	36.39
	100.00%	0.7287		100.00%

The composition of mineral is given according to these results by the formula Bi_6TeS_4 with a very good approximation. According

to the experimental and calculated results there is no doubt that the composition of the new mineral is Bi_6TeS_4.

Another part of the same polished section was also analysed. This sample was inhomogeneous according to microscopical investigations (10). The basis is bismuthine and emplectite. Beside there is to be found native Bi and bismuth telluride of significant quantity.

The result of qualitative analysis: Bi, Cu, Te, Fe, S.

The procedure was the following: the decomposition was carried out by nitric acid and bromine. The insoluble rest was filtered. The Bi, Fe and Te were precipitated by NH_4OH and $(NH_4)_2CO_3$. The filtrate contained copper and sulphate. The treatment of precipitate was as before; after precipitating of Te and Bi, Fe was determined. I determined first the sulphate from the filtrate, then from this filtrate, precipitating the excess of Ba with $(NH_4)_2SO_4$, I precipitated copper from a slightly acetic acideous medium with salicylaldoxim.

The analysis gave:

Bi	69.81%
Cu	7.98
Fe	1.90
Te	0.31
S	19.42
imp.	0.50
	99.92%

Bi_2TeS_2 (Csiklova — Ciclova):

Sztrókay (11) was the first who mentioned a member composed Bi_2TeS_2 which fits to the isomorph series of Bi_2Te_3-Bi_2Te_2S-Bi_2S_3. According to P. de Rubies the Bi-Te minerals are composed of the Bi_2S_3 and Bi_2Te_3 components. According to this opinion the composition of tetradymite is Bi_2S_3. 2 Bi_2Te_3 while the composition of the new member is 2 Bi_2S_3 . Bi_2Te_3.

An analysis of a polished section of ore gave a very interesting and remarkable result. This sample was found in Csiklova and was originally supposed to be a tetradymite.

The result of qualitative analysis: Bi, Te, Se, S and Fe.

	Weight %	Calculated to 100 %	Atomic ratio		Atomic %
Bi	67.76 %	68.10 %	0.3258	2.02	39.93%
Te	20.41	20.52	0.1608	1	19.70
Se	1.37	1.37	0.3295	2.04	40.37
S	9.97	10.01			
Fe	trace	—	0.8161		100.00 %
imp.	0.40	—			
	99.91 %	100.00 %			

Consequently the composition is Bi_2TeS_2. The ideal composition of the mineral according to the formula is:

	Weight %	Atomic %
Bi	68.56 %	40.02 %
Te	20.93	20.00
S(Se)	10.51	39.98
	100.00 %	100.00 %

The polished section of ore appeared quite homogeneous (10). Therefore the existence of the mineral — which had been found by *Sztrókay* (11) and the formula of which was also given by him on the basis of isomorphic relations — is proved by this analysis. Sztrókay proposed for denomination of this new mineral the name: grünlingite. This is not quite correct, because recent and older investigations carried out on grünlingite show, that grünlingite, just as joseite, is an indenpendent member of the series of Bi-Te minerals, having an invariable composition.

Cosalite — $Bi_2S_3 . 2\,PbS$ (Rézbánya — Baița):

I analysed a cosalite of origin of Rézbánya which had a very interesting and inusual composition. It was very remarkable that a part of S content was substituted by Se in this sample just as in the wittite. (The formula of wittite is $3\,Bi_2(S, Se)_3 . 5\,PbS$).

The result of qualitative analysis is: Bi, Pb, Ag, Cu, Fe, Se, S.

The procedure was as follows. The decomposition was carried out by nitric acid + bromine, then NH_4OH was carefully added to the solution without dilution until it lost its clearness. Afterwards ammonium carbonate was added to the solution and it was boiled for a short time. The precipitate was filtered: Bi, Pb, Fe and the insolubile rest. The filtrate was carefully evaporated. After adding a few drops of HCl the evaporation was repeated. The evaporated rest was dissolved in hot water and after the separation of silver the filtrate was put into a volumetric flask and the flask was filled. The amount on Se, Cu and sulphate were determined from three separate parts. of this solution.

	Weight %	Calculated to 100 %		Atomic ratio.		
Bi	43.09 %	46.38 %	0.2219	0.2219	1.03	2.06
Pb	22.86	24.60	0.1187			
Ag	3.74	4.02	0.0373	0.2153	1.00	2
Fe	1.74	—	—			
Cu	3.51	3.77	0.0593			
Se	6.57	7.06	0.0894	0.5314	2.06	4.92
S	15.16	14.17	0.4420			
imp.	3.05	—	—			
	99.72 %	100.00 %				

The sample used for analysis appeared quite homogeneous (10). Its formula according to the results of analysis is: $Bi_2Pb_2S_5$ or $Bi_2(Pb\,Cu_2\,Ag_2)_2(Se\,S)_5$. This latter would be more correct because it gives the composition more correctly. The giving of the formula is reasonable, because we find copper and silver among the components in almost every analyses.

A very similar analysis is given by Genth (12). He also pointed out Se in traces.

Summary:

1. Pure joseite and grünlingite samples were analysed to show that both minerals are independent members of the series of Bi-Te minerals, having an invariable composition.

2. We have to enter a new mineral into the series of Bi-Te minerals the composition of which is Bi_6TeS_4 according to my analyses.

3. I analysed a mineral found by Sztrókay. The composition was given by Sztrókay on the basis of calculations of lattice structure: Bi_2TeS_2. The result of my analysis verified the correctness of this formula.

4. I analysed a cosalite of origin of Rézbánya having very great Se content.

References:

1. *Clauder, O.:* Tellur meghatározása kristályos fém tellur és tellurdioxid alakjában. Budapest, 1931.

2. *Antal, J.:* A bismuth súlyszerinti meghatározása. Budapest, 1928.

3. *Koch, S.:* Néhány bismuth-ásvány Vaskőről. Budapest, 1930. Magyar Tud. Akadémia Mat. Term. Tud. Értesítő. Vol. XLVII. p. 219.

4. Chemiker Fachausschuss des Metall und Erz: Analyse der Metalle. Berlin, 1942. p. 279—298.

5. *Doelter, C.:* Handbuch der Mineralchemie. Leipzig und Dresden, 1925. IV./1. p. 853—861.

6. *Hintze, C.:* Handbuch der Mineralogie. Leipzig, 1904. I./1. p. 402—409.

7. Gmelin's Handbuch der anorg. Chemie 1940. Vol. 11. Te.

8. *Garrido, J. & Feo, R.:* Sur les sulfotellurures de bismuth. Bull. Soc. Soc. franc. Min. 61. 1938. p. 196.

9. *Peacock, M. A.:* Joseite from British Columbia. The Amer. Min. 1940.

10. *Koch, S.:* Bizmutásványok a Kárpát-medencéből. Szeged. 1948. Acta Min. Petr. Univ. Szegediensis. Tom. II.

11. *Sztrókay, K.:* Über den Wehrlit (Pilsenit). Budapest. 1946. Ann. Hist. Nat. Mus. Nationalis Hungarici. XXXIX. 4. p. 75—103.

12. *Genth, F. A.:* Contributions to Mineralogy. No. XXIV. 1885. Univ. of Pennsylvania.

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Láposbánya környékének geológiai felépítése.

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Nagybányától (Baia Mare) nyugatra kb. 8 km. távolságra lévő Láposbánya (Baitza) községtől közel északkelet-délnyugati irányban húzódó Láposbányai pataknak a völgye helyezkedik el az ismertetendő területnek a tengelyében. Északi határa a Botta-maretól (684 m.) északra lévő lomási völgy (Valea Limpege), majd a P. Petrisau (501 m.). Keleten a Vrf. Tuffoi (715 m.), Vrf. Copiasa (602 m.), Vrf. Luptescia (522 m.) a legmagasabb csúcsok a terület szélén és a Páprád völgyön keresztül éri el a déli üledékes zónát. Nyugaton a Botta maretól a Tirzán (535 m.) és a P. Soimuluin (513 m.) keresztül a Körte hegyig (344 m.) húzódó gerinc, délen pedig az alluviális üledék határolja.

Irodalmi adat, mely a vidék geológiai felépítésére nézve közelebbi felvilágosítást adna, kevés van.

Koch Antal (3) szerint a láposbányai völgytől keletre lévő terület és a Vörös patak közelebbi környéke nagyrészt dacitból